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Evaluating Multipollutant Exposure and Urban Air Quality: Pollutant Interrelationships, Neighborhood Variability, and Nitrogen Dioxide as a Proxy Pollutant

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Abstract

Background: Although urban air pollution is a complex mix containing multiple constituents, studies of the health effects of long-term exposure often focus on a single pollutant as a proxy for the entire mixture.

Objectives: We examined air pollutant concentrations and interrelationships at the intra-urban scale to obtain insight into the nature of the urban mixture of air pollutants. This will assist epidemiological studies that exploit spatial differences in exposure by clarifying the extent to which measures of individual pollutants, particularly NO₂, represent spatial patterns in the multipollutant mixture.

Methods: Mobile measurements of 23 air pollutants were taken systematically at high resolution in Montreal, Quebec, Canada, spread among 34 days in the summer, winter and autumn of 2009.

Results: We observed variability in pollution levels and in the statistical correlations between different pollutants according to season and neighborhood. Nitrogen oxide species (NO, NO₂, NO_x, and NO_y) had the highest overall spatial correlations with the suite of pollutants measured. Ultrafine particles (UFP) and hydrocarbon-like organic aerosol (HOA) concentration, a derived measure used as a specific indicator of traffic particles also had very high correlations.

Conclusions: The multipollutant mix varies considerably throughout the city, both in time and in space, and thus, no single pollutant would be a perfect proxy measure for the entire mix under all circumstances. However, based on overall average spatial correlations with the suite of pollutants measured, nitrogen oxide species appeared to be the best available indicators of spatial variation in exposure to the outdoor urban air pollutant mixture.

Introduction

Long-term cohort studies that examine effects of air pollution on human health depend on accurate estimates of pollution levels and their variability for large populations. Cohort studies that focus on large geographical domains or examine between-city differences in pollution levels typically have used relatively few central site measurements per city to characterize exposure contrasts (e.g., Dockery et al. 1993). In recent years, with an appreciation for within-city contrasts, there has been interest in the intra-urban scale. For such small scales central site monitors are inadequate for characterizing the full breath of exposure variations.

Several approaches have been taken to resolve the spatial variability in the intra-urban scales to assign exposures (HEI 2010), such as road-proximity, Land Use Regression (LUR), 3D air quality models, dispersion models, and hybrid modeling approaches (e.g., Sampson et al. 2011). These solutions are limited in that they depend on the accuracy and availability of input data (such as information on road networks, land use data, reported emissions, and meteorology) and the empirically-based models (LUR) typically predict the spatial pattern for a limited number of easily measured pollutants (e.g., NO₂, NO_x, black carbon) derived from a limited number of short measurement campaigns (typically two weeks) that may not account for the full variability within a season or a year. Nonetheless, associations between these predicted single pollutant spatial contrasts (most often NO₂) and health outcomes have been reported by a number of studies (e.g., Jerrett et al. 2009; Thiering et al. 2013).

It is recognized, however, that the air we breathe holds a mix of pollutants, and that the associations found in these health studies likely result from this mixture, and not the sole effect of

the proxy pollutant (Crouse et al. 2010). It is therefore necessary to examine the entire mix of pollutants (Dominici et al. 2010), addressing questions such as: How does the spatial pattern differ among pollutants? Do pollutants emitted from the same sources exhibit the same spatial patterns? Are statistical correlations between different pollutants constant over time? Are they constant over space? Such an evaluation of multi-pollutant patterns is important to better understand the magnitude of exposure assignment errors when using a single pollutant, the potential impact of such assignment errors on exposure-effect relationships and to ultimately understand the full effect of complex mixtures (Billionnet et al. 2012).

Measurements of multiple air pollutants were taken in the city of Montreal, Quebec, Canada, with a mobile lab at high spatiotemporal resolution over multiple days. This paper focuses on these outdoor air pollutant measurements and multipollutant spatial and seasonal contrasts with the aim of gaining a better understanding of multipollutant exposures in an urban environment. We examined multipollutant statistical correlations and seasonal variability in relationships among pollutants measured across Montreal including NO₂, carbonaceous particles and Ultrafine Particles (UFP) as pollutants related to traffic emissions in urban area and of considerable interest regarding potential health effects.

Our underlying hypotheses are that seasonal and spatial variations exist, not only in the ambient levels of different pollutants but also in the correlations between them, and that pollutants emitted from similar sources are correlated spatially.

Methods

A description of the study area, measurements, sampling strategy and spatial analysis is given in Levy et al. (2012). Briefly, mobile measurements of air quality and meteorological parameters were taken by Environment Canada's mobile lab, the Canadian Regional and Urban Investigation System for Environmental Research (CRUISER), in 2009. The study was conducted on the Island of Montreal, which has a population of 1.8 million. As with many large cities, air pollution in Montreal is spatially variable. In addition to traffic, pollution sources on the island include oil and gas refining, storage, and distribution facilities, and oil and gas heaters (in the winter) (Environment Canada 2008). Maps of the study area that include information on land uses and the locations of main roads and major point sources are provided in Figure 1.

The measurement campaign occurred during the winter (on 11 individual days, with the first on January 13th and the last on February 11th), summer (17 days between July 8th and September 3rd), and autumn (6 days between November 22nd and December 2nd) of 2009. In addition to reporting results according to season, we report results for the 34 measurement days combined. Measurements were done on both weekdays (31 days) and weekends (3 days). Twenty-three pollutants (see Supplemental Material, Table S1) were measured simultaneously at time resolutions ranging from 0.5 second to 2 minutes. Geo-location was recorded with GPS at 1-second intervals. All the measurements were organized according to 1-second intervals by averaging finer time resolution measurements and repeating values every second for measurements with coarser resolutions.

Two driving routes were systematically followed: 1) East Montreal; 2) Central and west Montreal. The east route was used most often (26 times, of which 11/11 were in the winter, 14/17 in the

summer and 1/6 in the autumn) due to a greater number of industrial facilities, particularly petrochemical, operating in that part of the city. Focus in this area also provided additional data on exposures relevant to an asthma panel study conducted just after our measurements and that involved children residing in East Montreal (Dobbin et al. 2011). The impact of industry on exposure and respiratory health was one of the underlying objectives of both our mobile measurement campaign and the panel study. On each mobile measurement day the entire route (east or west) was completed to insure that all measurement locations (i.e., road segments) were visited on the same days. However, the time of day that each segment was visited was varied across the day to avoid bias due to typical diurnal variations. Analysis of the measurements was done by first assigning each 1-second measurement to a road segment. For each road segment and each pollutant we then calculated the daily average value for each measurement day, the seasonal average value over all days in the measurement season, and the overall average value for all measurement days. A road segment was usually a line connecting two junctions. For each pollutant, measurements from a given road segment were included in the analyses only if there were > 100 CRUISER measurements per kilometer of the segment among all measurement days, with measurements on at least 3 different days. For example, out of a maximum of 1,200 possible road segments (i.e., this is the number of segments CRUISER drove on at least once), 855 segments met these criteria for NO₂ measurements, including 513 segments (60%) with measurements on ≥ 15 days, 624 (73%) that were 50-250 m in length, and 308 (36%) that were 50-100 m long (the modal length for all segments).

To our knowledge, several of the pollutants included in this analysis (Supplemental Material, Table S1) are unique to this study. NO₂ here is a specific measure of this species, as opposed to what is measured in regulatory air quality monitoring networks, which is typically biased by

interferences from other oxidized forms of nitrogen (e.g., peroxyacetyl nitrate – PAN, HNO_3 , N_2O_5) (Lee et al. 2011). Thus, NO_x is specifically $\text{NO} + \text{NO}_2$ because of the more accurate measurement of NO_2 . The instrumentation used also provided a direct measurement of total oxidized nitrogen species (NO_y), defined as $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_z$. This latter class of compounds, NO_z , represents the total quantity of nitrogen species that are more oxidized than NO_2 . NO_z is calculated from the direct measurements; $\text{NO}_z = \text{NO}_y - \text{NO}_x$. Given their highly oxidized form (e.g., peroxyacetyl nitrate – PAN, HNO_3 , N_2O_5) these ‘ NO_z compounds’ are of interest in terms of potential health effects (Brook et al. 2007). They are also a good indicator of photochemically-processed urban air, which builds up during warm season stagnation (Luria et al. 2005). Also, as an additional indicator of oxidizing pollutants we report O_x , which is the sum of NO_2 and O_3 . This measure remains constant when ozone is titrated by NO , which is a major reason for the observed spatial variability in ozone within cities. It is important to note that among the nitrogen-related compounds only NO and NO_y are measured directly, while NO_2 is obtained by measuring $\text{NO}_2 + \text{NO}$ with one instrument and subtracting the NO measured by a different instrument. Measurements obtained through this approach (i.e., a difference technique), which includes NO_2 and NO_z and those depending upon them (i.e., NO_x and NO_z) have larger uncertainties, compared to NO_y and NO .

The use of the Aerodyne Aerosol Mass Spectrometer (AMS) provided 2 minute resolution for the main contributors to PM_{10} mass; total organic matter (OM), sulphate (SO_4), nitrate (NO_3), ammonium (NH_4), and independent mass fragment (m/z) measurements across the full mass spectrum (m/z). Here we focus on $m/z57$ because of its relationship to fuel combustion, and on hydrocarbon-like organic aerosol (HOA), a derived measure calculated from the m/z fragments by a source apportionment model that provides an estimate of the total mass of organic particles

emitted from fossil fuel combustion (Levy et al., 2012). In cities, HOA is typically dominated by traffic exhaust.

Given that some emission sources vary by season (e.g., due to seasonal variation in heating or construction), and that some pollutants or their emissions are influenced by temperature, we hypothesized that there will be seasonal variation in ambient concentrations and multipollutant correlations, in addition to variation according to locations within the city. To test these hypotheses, we computed Pearson correlation coefficients between average levels of pollutants at corresponding road segments based on all available data, and separately for the winter, summer and autumn seasons. Moreover, we calculated correlations separately for three different residential neighborhoods where measurements were conducted approximately the same number of times over the same days and seasons (locations are shown in Figure 1B). The Anjou neighborhood is in proximity to two major roads and a major interchange; Riviere des Prairies (RdP), in the northwest part of the city, has much fewer industrial or traffic emission sources, but residents commonly use wood for residential heating (Gagnon et al. 2007); Point aux Tremble (PaT) is closer to the oil refineries and industrial emissions sources than the other two neighborhoods. While correlations are presented for all pairs of the pollutants measured, we focus on NO₂ and its relationship with BC and UFP, as all three are related to combustion sources and are commonly used as indicators of traffic air pollutant exposure. We also compare NO₂ with OM and HOA, as these particle species are more specific to traffic than BC and UFP, and are unique to this study. In addition, we also calculated the average correlation of each individual pollutant with all other pollutants. Although this is not a standard metric, we report it as an indication of how well each pollutant performs as an overall indicator of spatiotemporal variability in the urban air pollutant mixture.

Results

Seasonal variation in the relationship between NO₂ and particles

Mean concentrations of all pollutants were higher during winter versus summer measurement days, with the exception of ozone and the volatile organic compounds (VOCs: benzene, C3 benzene, toluene, and xylenes) (data not shown). Figure 2 shows plots of mean values of NO₂ vs. mean values of UFP, BC, OM, and HOA measured at corresponding road segments during summer and winter measurement days. Focusing on UFPs, the winter median and mean (~36,000 and ~41,000, respectively) are double the corresponding values measured in the summer (~17,000 and ~19,000, respectively), consistent with a greater buildup due to reduced evaporation in the winter. Although Pearson correlation coefficients (r_p) between UFPs and NO₂ are similar for the winter and summer (0.71 and 0.77, respectively), a 1-ppbv increase in NO₂ was associated with a larger increase in the number of UFPs during the winter than in the summer (2,281 UFPs/c³ vs. 1,384 UFPs/c³) (Figures 2a and 2b, respectively).

For BC, the correlation with NO₂ was smaller in winter than summer (r_p = 0.55 vs. 0.80, respectively), along with higher NO₂ mean and median in the winter (Figures 2c and 2d). In contrast with UFP, a 1-ppbv increase in NO₂ was associated with a larger increase in BC during the summer than in the winter (0.181 vs. 0.059 µg/m³) (Figures 2c and 2d, respectively). The median concentration of OM was higher during the winter than the summer (~3 vs. ~2.2 µg/m³), but its correlation with NO₂ was weaker in the winter (0.28 vs. 0.72) (Figures 2e and 2f). The median concentration of HOA also was larger in winter than in summer (0.82 vs. 0.40 µg/m³), but correlations with NO₂ were similar for both seasons (r_p ~0.53) (Figures 2g and 2h). As for UFPs, a

1-ppbv increase in NO₂ was associated with a larger increase in the HOA concentration during the winter than in the summer (0.035 vs. 0.018 µg/m³).

Multipollutant statistical correlations

Seasonal variability in multipollutant correlations and concentrations

Correlation matrix plots in Figure 3 show relatively strong correlations among the nitrogen species or classes (NO₂, NO, NO_x, NO_y and NO_z) based on combined data for all measurement days ($r_p = 0.70-0.99$, p -values < 0.001) (Figure 3A and Supplemental Material, Table S2).

In general, NO and NO_y were more strongly correlated with other pollutants than NO₂. For example, the overall correlation coefficients with UFP were 0.89 for both NO_y and NO, compared with 0.63 and 0.80 for NO₂ and NO_x, respectively) (Figure 3A and Supplemental Material Table S2). Average correlations with all other pollutants combined based on all measurement days (Supplemental Material Table S2) suggest that NO_y and NO ($r_{avg} = 0.53$) are slightly better overall indicators than NO₂ and NO_x ($r_{avg} = 0.40$ and 0.48 , respectively).

Other combustion-related pollutants, such as CO, O₃, UFP, OM, and HOA also show good correlations with most pollutants (r_{avg} between 0.46 and 0.55), except for SO₂, and the VOCs (which also have important non-combustion sources) (Figure 3). Interestingly, HOA (i.e, traffic-related particles) had the highest average spatial correlation with the other pollutants ($r_{avg} = 0.55$ for all measurement days combined) (Supplemental Material, Table S2). Of the gases measured, NO_y and CO had the strongest correlations with HOA ($r_p = 0.82$ and 0.84 for all days combined, respectively) (Figure 3).

For SO₂ and the VOC's there are almost no correlations with other species (e.g., $r_p < 0.17$ for SO₂). This is not surprising given that the spatial patterns observed for these pollutants show highest concentrations near industrial emissions and not along roads (see Levy et al. 2012). The VOCs are well correlated among themselves particularly in the autumn and winter seasons (Figures 3b and 3d, respectively). For example, r_p between Toluene and Xylenes is 0.75 and 0.78 in the autumn and winter, respectively (Supplemental Material, Tables S4 and S5, respectively). The different size fractions of particulate matter (PM₁₀, PM_{2.5}, and PM_{1.0}) show good correlations among themselves ($r_p = 0.56-0.85$, p -values < 0.0001) and lower correlations with the nitrogen oxides group ($r_p = 0.29-0.59$, p -values < 0.0001).

In general, correlation coefficients were higher for measurements in the summer compared with correlations for measurements over all days combined (Figures 3C and 3A, respectively), especially for the nitrogen species and CO, O₃, PM_{1.0}, UFP, BC, OM, Nitrate, and O_x (O₃ + NO₂). These correlations, however, decrease in the winter (Figure 3D). For example, the correlation between CO and NO was $r_p = 0.79$ for all days combined, 0.86 for summer measurement days, and 0.34 for winter measurement days. Correlations of PM₁₀ and PM_{2.5} with other pollutants were weaker in the summer and winter than for all days combined, while correlations of PM_{1.0} with other pollutants were highest in the summer and lowest in the winter.

Apart from the correlations between different pollutants, the mix of air pollutants in each season is also influenced by the mean concentration of each pollutant. The ratios between the mean concentrations among all road segments included for different seasons are shown in Figure 3e. Higher mean concentrations were found in the winter compared to the summer for almost all pollutants, with the exception of O₃, O_x and VOCs (Figure 3E). However, the magnitude of the

winter increase varied among pollutants, further indicating that the characteristics of the mixture are not stable between seasons.

Between-neighborhood variability in multipollutant correlations and concentrations

Figures 4A-I provide correlation maps of multipollutants for each neighborhood (same as Figure 3) focusing on nine pollutants, NO_2 , NO_x , NO_y , PM_{10} , $\text{PM}_{2.5}$, UFP, BC, SO_2 and HOA. Supplemental Material Figure S1A-C shows the correlations for all pollutants. The ratios given in Figure 4J indicate which neighborhoods have higher pollution levels and the extent to which pollutants vary differently among neighborhood.

While the correlations between nitrogen oxide species were high for all three neighborhoods (Figures 4A-C; Supplemental Material, Figure S1A-C), for each pollutant there were differences in the ratios of the average level in each neighborhood relative to the average for the study area as a whole (Figure 4J). For example, although the correlation between NO_x and NO in all three neighborhoods was about 0.97, the ratios of the average NO concentrations in each neighborhood relative to the entire study area were 0.64, 0.50, and 0.48 for Anjou, RdP and PaT, respectively, suggesting large spatial variation within the city, and considerably lower levels in the 3 neighborhoods than in other parts of the study areas. Average values of NO_x also were lower in the neighborhoods than in the study area as a whole, but the differences were less pronounced (ratios of 0.96, 0.75, and 0.68, respectively), suggesting less spatial variation in NO_2 between neighborhoods, and supporting neighborhood-specific variation in the NO and NO_2 mixture.

In general, across all three neighborhoods, average correlations of NO_2 , NO_x , and NO_y with all other pollutants (0.40-0.54, 0.44-0.55, and 0.43-0.54, respectively) were higher than average correlations of PM_{10} , $\text{PM}_{2.5}$, UFP, BC, SO_2 , or HOA with all other pollutants (Figure 4A-I).

Correlations for NO were also in these ranges. UFPs also had relatively high average correlations (0.38-0.51), while PM_{2.5} and SO₂ had low average correlations. Average correlations for HOA with all other pollutants were lower when calculated by neighborhood (correlations of 0.29-0.43) than based on all available data (0.55, Supplemental Material, Table S2), which included more measurements from main This further suggests that multipollutant relationships differ spatially with the nature of the sources playing a large role. In addition, average correlations for the combustion-related pollutants, (nitrogen species, UFP, BC, and HOA), which in most areas are strongly linked to traffic, were highest in the highway-impacted Anjou neighborhood (average values 0.43-0.55). In contrast with combustion-related pollutants, PM_{2.5} had a higher average correlation with other pollutants in the low traffic, less industrially influenced Riviere des Prairies neighborhood than in the Anjou neighborhood (0.39 versus 0.20). Lower average correlations with other pollutants for PM_{2.5} than other pollutants in all locations may at least partly reflect the low spatial variation of PM_{2.5} over the study area relative to other pollutants.

While in Levy et al. (2012) we show how SO₂, benzene, and toluene have the highest concentrations in proximity to the petrochemical emission sources, here we examine the impact of the petrochemical industry and the use of SO₂ as an indicator of these emissions in a quantitative approach by examining the statistical correlations of SO₂ and other pollutants at different locations. We observed large differences among areas of the city for SO₂ (as well as benzene and toluene), with mean SO₂ levels in the Point aux Tremble neighborhood that were 2.2 times higher than mean levels in the study area as a whole (Figure 4J). Figure 4H further isolates the correlation of SO₂ with the other pollutants by neighborhood, demonstrating different exposure patterns at different parts of the city. Interestingly, in the area closest and most impacted by the petrochemical industries (Point aux Tremble), SO₂ exhibits the poorest correlation with the other pollutants (r_{avg}

= 0.16). In contrast, in Anjou, which is in a different direction from the petrochemical industries with respect to the prevailing westerly winds and further away (Figure 1), the correlations increase ($r_{\text{avg}} = 0.27$).

Discussion

Our results demonstrate that there can be large differences in the intra-urban spatial distributions of pollutants. Among the pollutants commonly used as human exposure indicators for epidemiological studies, correlations with other pollutants were relatively high for NO, NO₂, NO_x, and UFP, while correlations with PM_{2.5} and SO₂ were relatively low. Although all these nitrogen species/classes were measured with the same method (high time resolution chemiluminescence), which may tend to enhance their inter-correlations relative to those with other pollutants, this cannot entirely explain these correlations. Although our findings suggest that total oxidized nitrogen and HOA also may be good indicators of the mixture we measured, they are not included in typical monitoring network data, and inexpensive techniques to measure them are currently not available. Our results also showed seasonal differences in the correlations and relationships between pollutants, along with differences in their average concentrations.

The main reason for the spatial differences in correlations among pollutants was found to be the difference in their emission sources. Some pollutants are more linked to roads and traffic emissions (NO, NO₂, UFP and HOA), others to industrial sources (SO₂ and Benzene) and others to smaller, localized activities (Levy et al. 2012). Even for pollutants associated with common sources, such as SO₂ and benzene, which are released from study area refineries, we observed small-scale differences in spatial patterns which reflect differences in the volumes of emissions from different sources (Environment Canada 2008), differences in the specific sources of

emissions within an industrial complex (i.e., location and height), and differences in dispersion due to differences in their reactivity and physical characteristics. Thus, depending upon distance from the source and concentration averaging time, measurements may imply that certain pollutants co-vary when they are not physically linked. Consequently, there is potential for their exposure patterns within the population to differ and thus cause exposure misclassification. Although SO₂ has been used as an indicator of exposure to refinery emissions in previous studies (Smargiassi et al. 2009) our observations suggest that it may not be an accurate indicator to specific aspects of the refinery emissions that could be more directly responsible for an adverse health effect in the Montreal study area.

Examining the nature of the relationship among pollutants in the mixture we focused on NO₂ and other traffic-related pollutants. We found a larger number of UFPs for each ppbv increase of NO₂ in the winter compared to the summer. Thus, in areas where NO₂ is higher there are greater amounts of UFPs in winter than in summer. This may reflect reduced evaporation of UFPs co-emitted with NO_x when temperatures are colder (Olivares et al. 2007). HOA, a measure of traffic-related particles, were also more strongly associated with NO₂ concentrations in winter than in summer, possibly due to a similar dependence on temperature.

In contrast with UFPs, associations between BC concentrations and NO₂ were stronger in the summer than in the winter. This suggests a source for NO₂ that emits less BC and /or a source for BC that emits less NO₂ in the winter. An emitter to explain the former is natural gas heating, which, although not the main source for heat, is used in Montreal (Statistics Canada 2010). For the latter, the lower combustion temperatures of wood burning for residential heating is a possible reason for a higher BC to NO_x emission ratio in winter, particularly in East Montreal (Gagnon et al. 2007). The higher wintertime OM concentration along with a lower OM correlation with NO₂

further suggests an additional source for particles in the winter that does not produce as much NO_x .

Beyond seasonal variation in emissions, there are two main reasons for the seasonality in pollution levels and correlations. First is the stable vertical structure in the lower atmosphere in the winter (Bergeron and Strachan 2012). Second, lower temperatures and reduced solar radiation in winter result in less photochemical activity, causing, for example, slower conversion of NO to NO_2 and NO_2 to NO_3 and therefore more buildup of primary pollutants. Conversely, the photochemical production of ozone is higher in the summer due to stronger solar radiation, while UFPs and at least some portion of the traffic particle mass (HOA) evaporates faster or do not form or condense in as high abundance as vehicle exhaust cools when ambient temperatures are higher in summer.

Differences in the seasonal behavior of air pollutants result not only in different levels of exposure to individual pollutants during each season, but also in different correlations between pollutants, which may also vary depending on their sources, thus reducing the accuracy of individual pollutants as proxy measures of chronic ambient air pollution exposures in urban areas. When combined with seasonality in population behavior, consideration of the seasonal differences in multipollutant behavior presented here can help lead to more-informed assessments of exposure contrasts in epidemiological studies. For example, the implication of the different NO_2 -UFP slopes between summer and winter is that if the association found between NO_2 and health outcomes is due to UFP in the air pollution mix, then NO_2 should show a stronger effect in the winter. This could be observable assuming people spend the same amount of time outdoors in both seasons and if the indoor-outdoor air exchange rates do not vary between seasons. Nevertheless, the conclusion to be drawn is that NO_2 has a non-constant relationship during the year with some of the suspected causative pollutants. These are additional sources for uncertainty in epidemiological analysis that

need to be addressed in order to confidently identify the pollutants or sources that are more responsible for the observed associations.

Given the limited number of pollutants available at monitoring sites to inform exposures for most health-related studies, it is important to consider their representativeness, particularly for NO₂. However, few studies have taken spatial measurements of multiple pollutants to be able to quantitatively examine the associations of NO₂ and other pollutants. Our results imply that while no single pollutant will capture the urban-scale variability in chronic human exposures to the air pollution mix as a whole, to a subset of exposures (e.g., traffic-related pollutants), nitrogen species (NO, NO₂, NO_x, and NO_y), and, to a lesser extent, UFP, may be considered reasonably accurate proxy measures. This helps explain why estimates of chronic exposures to traffic related air pollution by LUR models for NO₂ has been useful in epidemiological studies. The higher correlations of NO_x and NO_y to other pollutants also suggest that detailed spatial maps for these pollutants may be more advantageous than NO₂ for health studies, especially if the focus is on traffic-related air pollutants.

Several limitations should be discussed with respect to this study. One limitation is the representativeness of our road segment averages to chronic exposure conditions given the limited number of days and exclusion of evenings and nights. To assess these limitations our averages were compared to the actual 2009 annual averages in Levy et al. (2012). As expected, a small sample of visits could not perfectly match the annual average, but at the available monitoring sites CRUISER's averages were within 25% of the observed values for NO_x, NO₂, O₃, and PM_{2.5} and within 40% for CO and 31% for SO₂. The average ratio of CRUISER to the network NO_x average was 0.96, suggesting that our mobile measurements attained a reasonable amount of long-term representativeness, while also covering a large range of urban settings.

The number of road segments meeting our criteria for computation of an average concentration varied by season and pollutant. This could affect our comparisons of correlations and regression results in terms of the magnitude and significance of the differences shown. For this reason we expect that the most robust multipollutant correlations were those based on all of the data combined. Although a large number of the seasonal correlations were found to be significant, we did not test for significant differences among corresponding estimates by season or neighborhood. Another potential limitation is the restriction of our measurements to roads, which may not represent pollution levels at locations where people spend their time.

Conclusions

Multipollutant correlations presented in this paper characterize, both spatially and seasonally, the potential extent of the variability in the mix of air pollutants in urban areas. Not only do average levels of individual pollutants change from season to season, but correlations between pairs of pollutants can also vary by season. Furthermore, spatial correlations vary across the city. Consequently, no single pollutant can serve as a perfect proxy for the air pollution mix. However, among the more easily measured and often readily available pollutants, nitrogen species (NO , NO_2 , NO_x) continue to be the “best compromise” as proxy measures of urban-scale variability in chronic exposures to complex urban air pollution mixtures. In cities, such pollutants are strongly linked to traffic emissions, but are not solely due to this source.

Conveying the tremendous amount of information that can be obtained through mobile surveys and extracting useful insights represents a challenge. This paper and Levy et al. (2012) provide examples of approaches that may be used to meet this challenge in the context of understanding chronic exposure. This work helps confirm the degree of multi-scale complexity in urban outdoor

air pollutant levels, and the likelihood of substantial variability in individual exposures. Clearly, attempts to relate health endpoints to specific sources or industries and their mixtures through epidemiological studies must take this variability into consideration when assigning exposures and interpreting results.

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Figure Legends

Figure 1. (A) Map of the study area showing land use types and CRUISER's east (blue) and west (red) routes. (B) Higher resolution map showing the three neighborhoods of Anjou, Riviere des Prairies, and Point aux Tremble, major roads, land use types, major emission sources, and CRUISER's stop sites for the smaller area outlined in panel A. (C) The density of measurements per kilometer of road segment (measurements/km) based on all measurements combined.

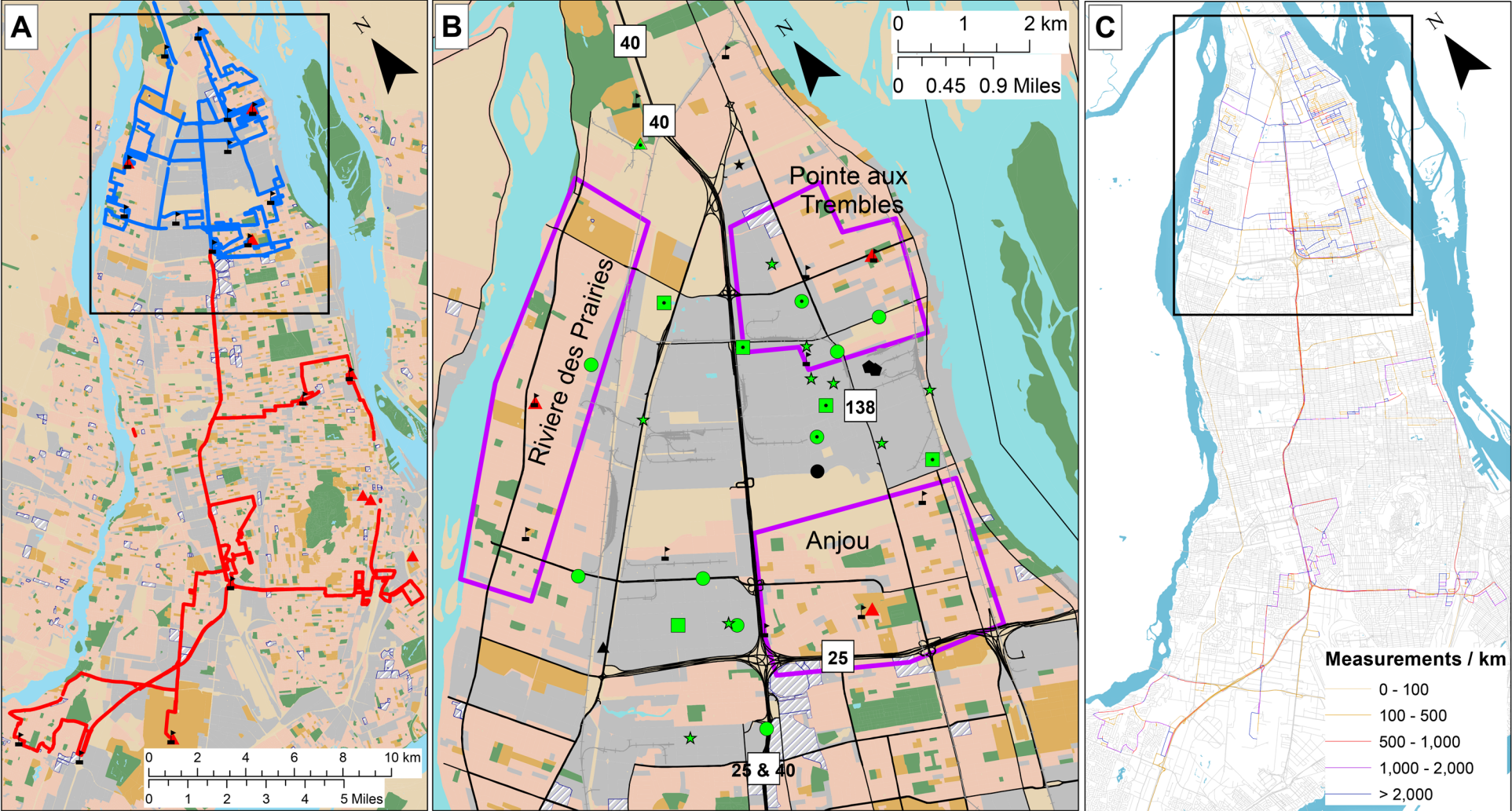
Figure 2. Scatter plots of UFP, BC, OM, and HOA (y -axes) vs. NO_2 (x -axes) for summer and winter measurements, with boxplots on the top edge of each panel indicating the distribution of measurement data for NO_2 , and boxplots on the right edge of each panel indicating the distribution of measurement data for the other pollutants. Each point in the scatterplots represent the average measurement at a road segment with at least 100 measurements per km on three or more days. Box plots show the mean, median, high and low quartiles, 1.5 IQR range and outliers (red square, blue line, black box, red notches and points, respectively). r is the Pearson's correlation coefficient, p is the p -values of the correlation and N is the sample size. The variable sample sizes (N) between seasons and pollutant pairs are due to different numbers of measurement days and rates of data loss (i.e., due to QA/QC procedures and our criteria for data completeness for each segment). The equation at the top of each panel is the linear regression fit of the two pollutants, with the slope and intercept of each pair.

Figure 3. Pearson correlation coefficients for pairs of pollutants for all measurement days combined (A, 34 measurement days), and for measurement days in the autumn (B, 6 days), summer (C, 17 days), and winter (D, 11 days), with non-significant correlations ($p > 0.05$) indicated by a black dot, and the magnitude of each correlation indicated on the color bar to the

right. Numeric data corresponding to the 4 panels are provided in Supplemental Material, Tables S2-S5. (E) Ratios of mean pollutant levels measured in the summer and winter compared with mean values based on all measurement days combined, and ratios of mean pollutant levels measured in the winter compared with the summer.

Figure 4. (A-I) Pearson correlation coefficients between pairs of pollutants according to neighborhood [Anjou, Riviere des Prairies (RdP), and Point aux Tremble (PaT)] for selected pollutants indicated at the top of each panel and mean absolute values of correlations between the selected pollutants and all other pollutants measured (r_{avg}) according to neighborhood for all measurement days combined. (J) Ratios of the average correlations for each pollutant with all other pollutants in each neighborhood to the average correlation for the same pollutant with all other pollutant over the entire study area. All data are based on all measurement days combined. Non-significant correlations ($p > 0.05$) are indicated by a black dot, and the magnitude of each correlation is indicated on the color bar to the right.

Figure 1



Legend

NPRI emission sources

- Cement and Lime
- ★ Chemicals
- ▲ Electricity
- ▲ Iron and Steel
- Manufacturing, Other

- ◆ Metals (Except Aluminum, Iron & Steel)
- Mining and Quarrying
- Oil and Gas Pipelines and Storage
- Petroleum and Coal Refining and Mfg.
- ★ Plastics and Rubber

Roads

- Roads
- Railway
- CRUISER's Routes
- East
- West

Selected neighborhoods

- ▲ CRUISER's stop sites
- ▲ AQ site

Land Use

- Commercial
- Government & Inst.
- Open Area

- Parks and Recreational
- Residential
- Resource and Industrial
- Waterbody

Measurements / km

- 0 - 100
- 100 - 500
- 500 - 1,000
- 1,000 - 2,000
- > 2,000

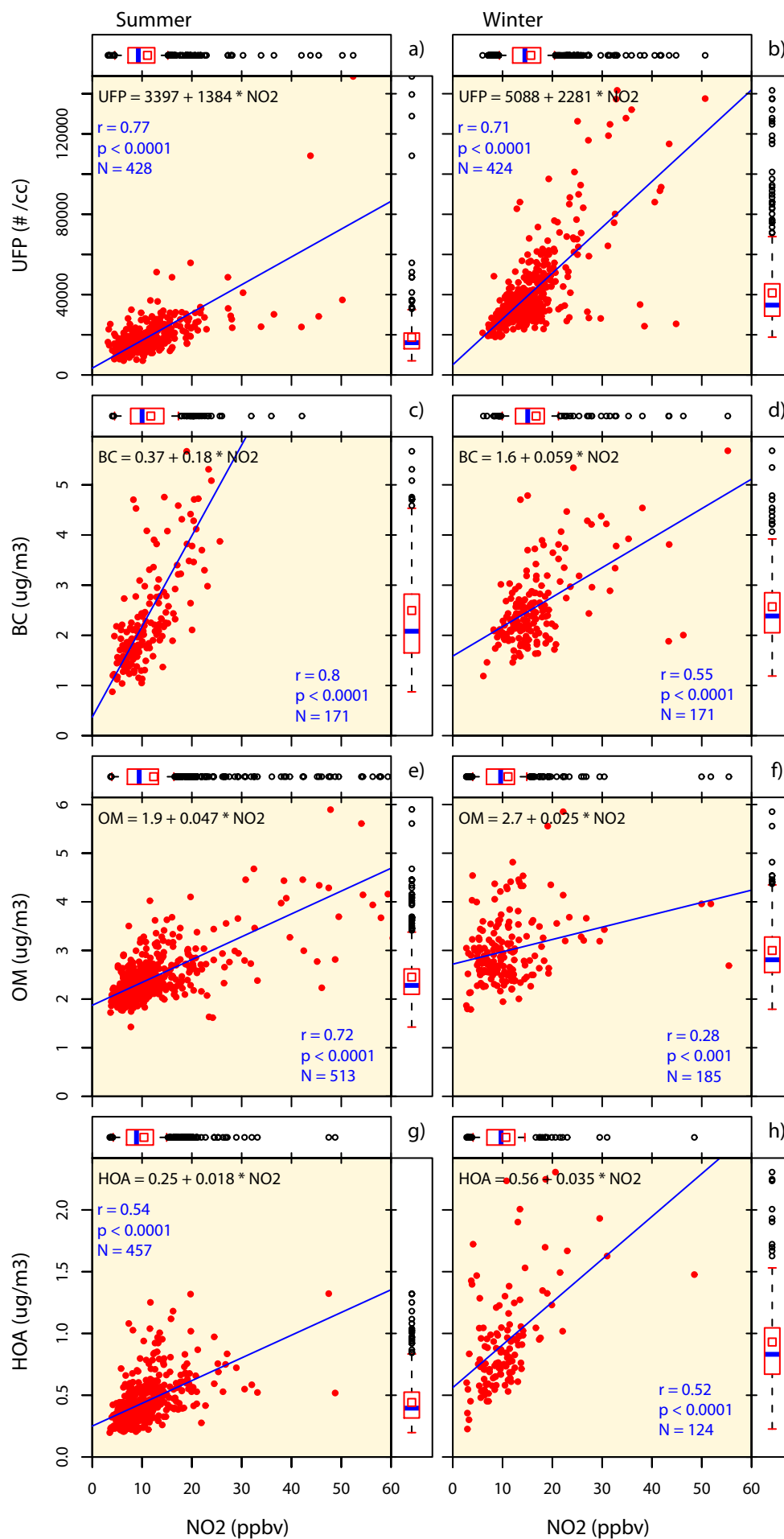


Figure 2.



Figure 3.

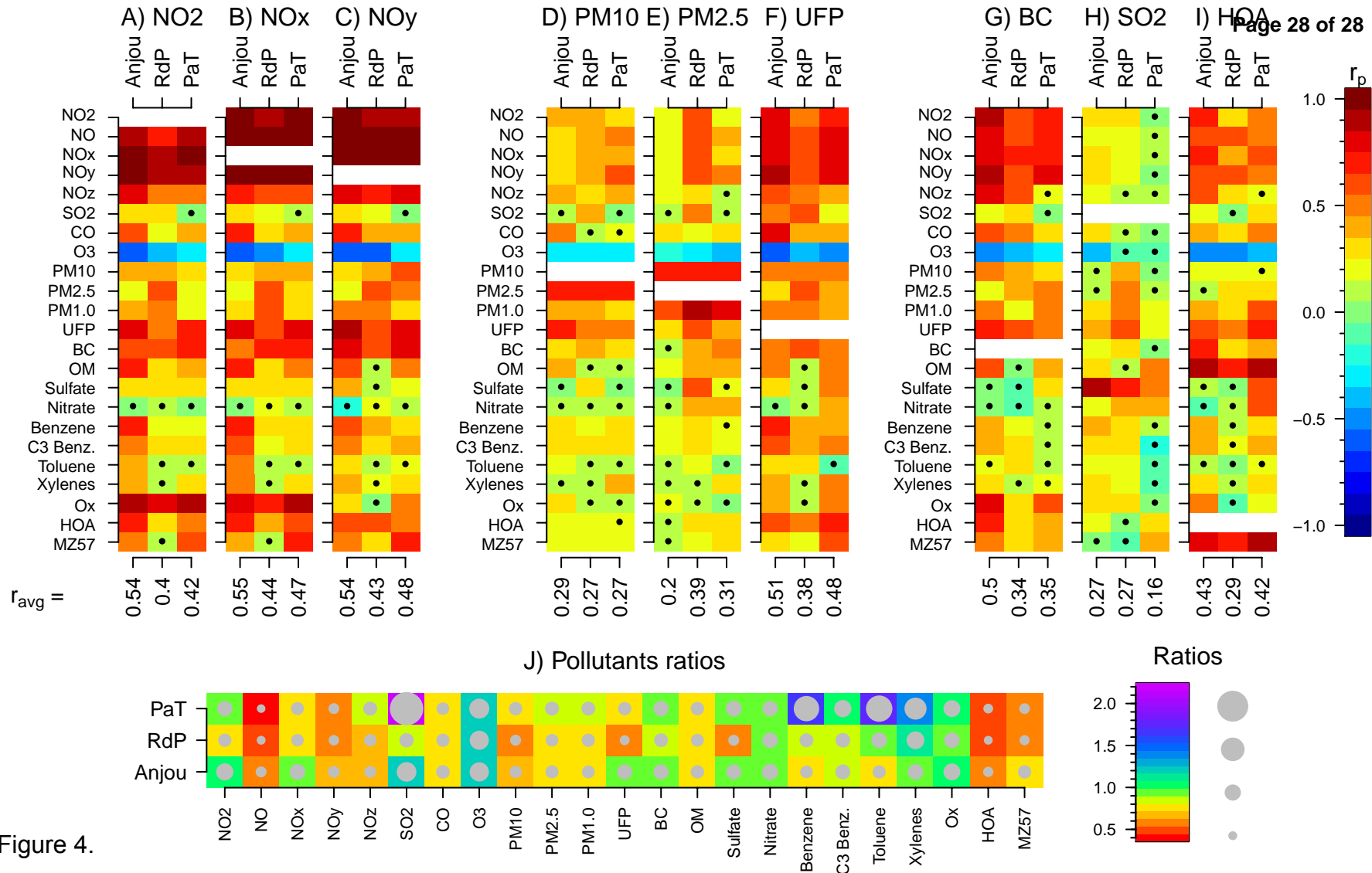


Figure 4.